

## MISORIENTED EPITAXIAL GROWTH OF (111)CoSi<sub>2</sub> ON OFFSET (111)Si SUBSTRATES

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### ABSTRACT

Single crystal epitaxial films of CoSi<sub>2</sub> were grown by MBE on various (111)Si single crystal substrates, whose surfaces were purposely tilted towards the  $\langle 1\bar{1}0 \rangle_s$  direction by small angles  $\phi_s$ ,  $0^\circ \leq \phi_s \leq 4^\circ$ , measured between the surface normal and the  $\langle 111 \rangle_s$  direction of Si. The actual offset angle,  $\phi_s$ , was determined by back Laue reflection method. The average perpendicular strain of the CoSi<sub>2</sub> epilayer,  $\epsilon^\perp$ , and the  $\langle 111 \rangle_f$  orientation of the epitaxial CoSi<sub>2</sub> film were determined by double crystal diffractometry. We find that the misorientation angle,  $\alpha$ , measured between the Si  $\langle 111 \rangle_s$  and CoSi<sub>2</sub>  $\langle 111 \rangle_f$  directions, increases linearly with the offset angle,  $\phi_s$ , up to  $\phi_s = 4^\circ$ . A simple geometrical model is developed which predicts that  $\alpha = \epsilon^\perp \times \tan \phi_s$ . The model agrees quantitatively with the experimental data. The equivalent strain energy associated with the misorientation is approximated by that of a low angle tilt boundary. The misorientation angle  $\alpha$  of the equilibrium state, determined by minimizing the total strain energy of the epitaxial film, is nonzero in general.

### INTRODUCTION

Epitaxial silicides on Si, NiSi<sub>2</sub>/Si and CoSi<sub>2</sub>/Si, have been intensively studied in the past few years. Systematic investigations of the silicide and Si interface by HRTEM<sup>[1]</sup> have revealed some important properties of the epitaxial silicide film, such as the atomic arrangement at the interface, the existence of two types of the epitaxial silicide A and B<sup>[2]</sup>, the characteristics of the interfacial dislocations and associated steps<sup>[1]</sup>, and the controlled growth of pure type A or B NiSi<sub>2</sub> film by template technique.<sup>[3,4]</sup>

The morphology associated with a Si surface that is slightly misoriented from a Si (111) plane has been studied by LEED<sup>[5]</sup>. A Si surface whose normal,  $\hat{n}$ , is tilted toward  $\langle 1\bar{1}0 \rangle_s$ , consists of clusters of steps of height  $d_{(111)}$ , whose edges are parallel to  $\langle 11\bar{2} \rangle_s$ . The metallurgical and crystallographic implications of this complex surface structure have not been fully explored.

In this paper, we investigate the effect of a misorientation of the (111)Si substrate on the misorientation of the epitaxial (111)CoSi<sub>2</sub> film. Based on current knowledge of the interfacial structure of the epitaxial (111)CoSi<sub>2</sub> and (111)Si system and our experimental data, we develop a geometrical model to describe the misorientation between the  $\langle 111 \rangle_f$  and  $\langle 111 \rangle_s$  directions. The quantitative relation between the relevant geometrical quantities,  $\alpha$  and  $\phi_s$ , is derived by imposing the equality of two lengths at the interface. We further study the elastic properties and interface dislocations associated with this misorientation, in an attempt to understand the physics behind the phenomenological model. Minimization of the strain energy in the epitaxial layer is taken as a criterion for the equilibrium state. Using Read-Schockley's formula for the strain energy of the low angle tilt boundary as an approximation of the equivalent strain energy for the misorientation, we show that for a general heteroepitaxial system, the total strain energy is reduced by a certain amount of misorientation. In other words, the misoriented state is stable.

† Subscripts *s* and *f* refer to substrate and epitaxial film, i.e., Si and CoSi<sub>2</sub>, respectively.

## EXPERIMENTS AND RESULTS

A set of mechanically polished (111)Si wafers of three typical offset angles,  $\phi_f \approx 0.1^\circ, 2^\circ, 4^\circ$ , were used as the substrates for studying the misorientation effect. All wafers were cut towards  $\langle 1\bar{1}0 \rangle_s$  direction with offset angles,  $\phi_s$ . The Si surface was cleaned by the usual RCA procedure. The residual oxide layer was stripped off by either flash heating to  $900^\circ\text{C}$  or Si beam self cleaning in the UHV chamber. The base pressure was  $10^{-10}$  Torr. A stoichiometric film of  $\text{CoSi}_2$  was deposited on the Si substrate heated to about  $550^\circ\text{C}$  in a vacuum of  $10^{-9}$  Torr, by keeping the Si:Co ratio close to 2:1.

Samples of single epitaxial (111) $\text{CoSi}_2$  layers on (111)Si, ranging in thickness from  $100\text{\AA}$  to  $2000\text{\AA}$ , were prepared under similar growth conditions. RBS and channeling were employed to characterize the stoichiometry, thickness, and crystal quality of the epitaxial layer. Some samples were analyzed by both plane-view and cross-sectional TEM to reveal pinholes, dislocation networks and interface structures. Back diffraction Laue x-ray was used to measure the offset angle,  $\phi_s$ . The x-ray double crystal diffractometry (DCD) from symmetrical (111) and (333) diffraction planes were used to obtain the average perpendicular strain,  $\epsilon^\perp$ , and the misorientation angle,  $\alpha$ .

Epitaxial  $\text{CoSi}_2$  films grown on Si(111) are usually preferentially type B. Some plausible explanations based on the difference of the dislocation characteristics of type A and B films have been proposed<sup>[6]</sup>. All of our samples are pure type B. This makes the x-ray rocking curve measurements from non-symmetrical diffraction planes, e.g., (311) or (422), very difficult. A direct experimental determination of the average parallel strain,  $\epsilon^\parallel$ , of the epilayer has thus not been performed. Instead,  $\epsilon^\parallel$  was estimated from the relation

$$f = \left( \frac{1-\nu}{1+\nu} \right) (\epsilon^\perp + \frac{2\nu}{1-\nu} \epsilon^\parallel), \quad (1)$$

where  $f = -1.2\%$  is the lattice misfit between  $\text{CoSi}_2$  epilayer and Si substrate, and  $\nu$  is Poisson's ratio of  $\text{CoSi}_2$  ( $\nu = 0.28$  was used).

In the following paragraph, we briefly describe the procedure for obtaining  $\epsilon^\perp$  and  $\alpha$  from the rocking curves of the symmetrical diffraction planes for the samples with offset angles. In general, the diffraction vector  $\hat{g}_f$  of the epilayer is not necessarily in the plane of the diffraction vector  $\hat{g}_s$  of the substrate and the surface normal  $\hat{n}$ . Therefore, at least three measurements are needed to determine the average perpendicular strain,  $\epsilon^\perp$ , and the orientation of the diffraction vector,  $\hat{g}_f$ , of the epilayer. For the samples we analyzed, where the Si surface normal  $\hat{n}$  was tilted towards the  $\langle 1\bar{1}0 \rangle_s$  direction, we found that  $\hat{g}_f$  lies in the plane of  $\hat{g}_s$  and  $\hat{n}$  (i.e., in the  $(11\bar{2})$  plane). If the sample is mounted such that  $\hat{g}_s$  lies in the plane of the incident beam  $\hat{k}_i$  and the surface normal  $\hat{n}$  (in other words, the sample is aligned so that  $\hat{k}_i$  lies in the  $(11\bar{2})$  plane), only two measurements are necessary [Fig.1]. From the two rocking curves, the average perpendicular strain,  $\epsilon^\perp$ , and the misorientation angle,  $\alpha$ , can be obtained [Fig.2],

$$\epsilon^\perp = -k_1^{-1} \times \frac{\Delta\theta_I + \Delta\theta_{II}}{2}, \quad (2)$$

$$\alpha = \frac{\Delta\theta_I - \Delta\theta_{II}}{2}, \quad (3)$$

where  $k_1 = \tan \theta_B$ ,  $\theta_B$  is the Bragg angle, and  $\Delta\theta_{I,II}$  is the rocking curve peak separation for the two diffraction configurations I,II of Fig. 1. Results from back reflection Laue and DCD analyses are summarized:

(1) The  $\langle 111 \rangle$  direction of the  $\text{CoSi}_2$  film lies between the surface normal  $\hat{n}$  and the  $\langle 111 \rangle$  direction of the Si substrate [Fig.1, 2].

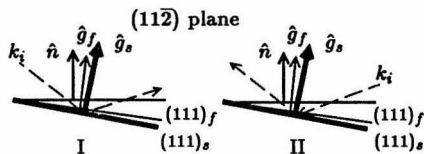


Fig.1 Configurations of the two symmetrical x-ray diffraction used to measure the misorientation angle  $\alpha$  between  $\hat{g}_f$  and  $\hat{g}_s$ .

(2) The average perpendicular strain,  $\epsilon^\perp$ , of the  $\text{CoSi}_2$  film, is essentially constant with increasing film thickness  $t_f$  from 100 Å upto 2,000 Å [Fig.3], with an average value of  $\sim -1.75\%$ . On the other hand, the van der Merwe model<sup>[7]</sup> predicts that the strain will decrease with the introduction of misfit dislocations which is energetically favorable when the thickness of the epilayer is larger than the critical thickness  $t_c$  ( $t_c \leq 100$  Å for  $\text{CoSi}_2/\text{Si}(111)$ ). † This discrepancy may indicate that the relatively large strain state in the  $\text{CoSi}_2$  epilayer grown under our growth conditions (relatively low temperature of  $\sim 550^\circ\text{C}$ ) is metastable. The strain relaxation to the thermal equilibrium value by the nucleation and multiplication of the misfit dislocation is inhibited by kinetics<sup>[8]</sup>.

(3) The magnitude of the misorientation angle,  $\alpha$ , is proportional to the offset angle,  $\phi_s$ . It does not depend on the layer thickness  $t_f$ .

## DISCUSSION

The atomic configuration of the silicide/Si interface has been revealed by HRTEM<sup>[5]</sup>. At the silicide/Si(111) interface, two types of Burgers vector,  $\frac{a}{2}[1\bar{1}0]$  and  $\frac{a}{6}[11\bar{2}]$ , have been identified<sup>[9]</sup>. In particular, Burgers vector of type  $\frac{a}{6}[11\bar{2}]$  can exist only in a type B film without a stacking fault. Furthermore, dislocations of this type are associated with a step of height  $d_{(111)}$  at the silicide and Si(111) interface. The step results in an equivalent displacement along the  $\langle 111 \rangle_s$  direction<sup>[1]</sup>.

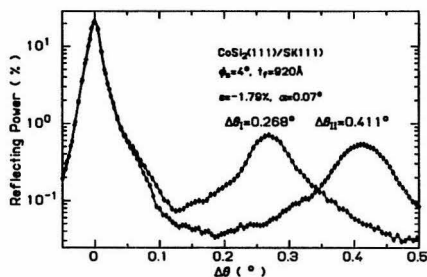


Fig.2 Two x-ray rocking curves from the (111) diffraction planes of same  $\text{CoSi}_2/\text{Si}$  bicrystal.

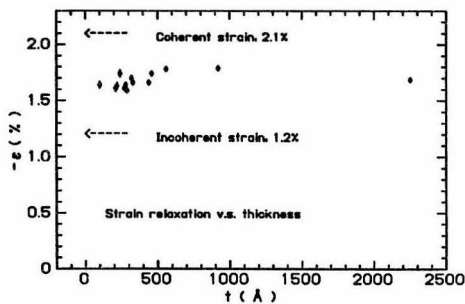


Fig.3 The relaxation of the average homogeneous perpendicular strain in the  $\text{CoSi}_2$  film v.s. the film thickness.

† The strain,  $\epsilon$ , in this paper refers to strain relative to the substrate,  $\epsilon \equiv \frac{\bar{a}_f - a_s}{a_s}$ , where  $\bar{a}_f$  is the average homogeneous lattice spacing of the epilayer.

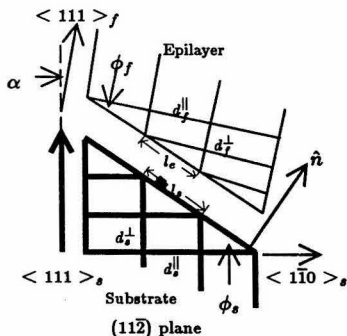


Fig.4 Graphic representation of the geometrical model. "Length Matching" condition is  $l_e = l_s$ .

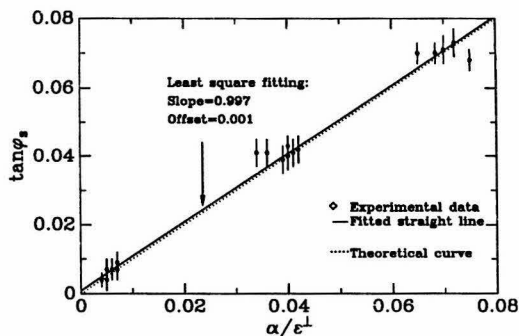


Fig.5 The functional relationship between the misorientation angle  $\alpha$  and the offset angle  $\phi_s$  of CoSi<sub>2</sub>/Si(111) bicrystal.

Based on the experimental findings and current knowledge about the interfacial structure of the epitaxial silicide and Si (in particular, CoSi<sub>2</sub> on Si(111)), we propose a simple geometrical model to relate the geometrical quantities of the epilayer and substrate interface. In the ideal case of coherent growth, by imposing "length matching" across the interface[Fig.4], we obtain the following relations

$$l_e = \frac{d_f^\parallel}{\cos \phi_f} = \frac{d_s^\parallel}{\cos \phi_s} = l_s, \quad \text{or} \quad l_e = \frac{d_f^\perp}{\sin \phi_f} = \frac{d_s^\perp}{\sin \phi_s} = l_s, \quad (4)$$

which after some calculation, gives for the misorientation angle  $\alpha (\equiv \phi_f - \phi_s)$

$$\alpha = \epsilon^\perp \times \tan \phi_s \quad (5a)$$

and

$$\epsilon^\parallel = -\epsilon^\perp \times \tan^2 \phi_s, \quad (6a)$$

to the first order in  $\alpha$  for small  $\alpha$ , where  $\epsilon^{\perp,\parallel} = (d_f^{\perp,\parallel} - d_s^{\perp,\parallel})/d_s^{\perp,\parallel}$  is the x-ray strain. In a general case where there exists misfit dislocation arrays at the interface, similar results can be derived,

$$\alpha = \epsilon^\perp \times \tan \phi_s \quad (5b)$$

and

$$\epsilon^\parallel = -\delta - \epsilon^\perp \times \tan^2 \phi_s, \quad (6b)$$

where  $\delta$  is the strain relaxation from the misfit dislocation. Equation (5b) predicts that  $\alpha$  is proportional to  $\phi_s$  for small offset angles  $\phi_s$  ( $< 45^\circ$ ). The least squares fitted linear function from the experimental data are compared with equation (5b). Excellent agreement is obtained [Fig.5].

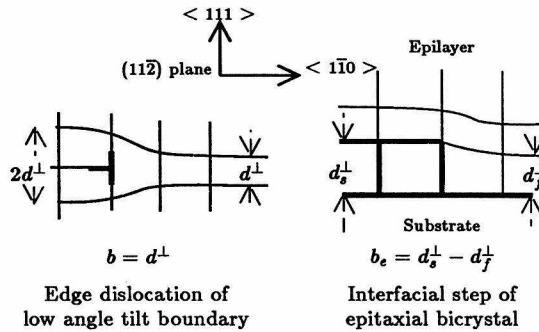


Fig. 6 Schematic diagram demonstrating the similarity between a low angle tilt boundary and an epilayer on a stepped substrate.

To understand better the driving force for the misorientation generation, we consider the strain energy of the epilayer and discuss the stability of the strain state with misorientation for epitaxial bicrystal. To estimate the equivalent strain energy due to the misorientation, we assume equivalence between our bicrystal interface and the low angle grain boundary in the bulk crystal [Fig.6]. In this simplified picture, the stress field of the step is approximated by the stress field of the edge dislocation with an equivalent Burgers vector,\*

$$b_e = d_s^\perp - d_f^\perp, \quad (7)$$

pointing in the surface normal direction. Furthermore, we approximate the step clusters by the edge dislocation arrays (They both have no long range stress field). Therefore, the misorientation angle is

$$\alpha = \frac{b_e}{D} = \epsilon^\perp \times \tan \phi_s, \quad (8)$$

where  $D$  is the average spacing between two interface steps. The corresponding strain energy per unit area is<sup>[10]</sup>

$$E_m = \frac{Gb_e}{2\pi(1-\nu)} \times \alpha(A - \ln \alpha), \quad (9)$$

where the parameter  $A$  depends on the "core" energy at the step. The total strain energy per unit area in the film contains three parts, the elastic energy from the homogeneous strain, the misfit dislocation energy, and the misorientation energy†

$$E_t = E_s + E_d + E_m. \quad (10)$$

The energy expression for both homogeneous strain and dislocations are well known<sup>[11]</sup>,

$$E_s = 2G\left(\frac{1+\nu}{1-\nu}\right) \times t_f \times (\delta + f + \epsilon^\perp \tan^2 \phi_s)^2, \quad (11)$$

\* The equivalent Burgers vector is not a lattice translation vector in this case.

† We assume that the interaction energy between the misfit dislocation and the misorientation is small compared to their self energy, and neglect it in the calculation.

and

$$E_d = \frac{Gb\delta}{2\pi(1-\nu)} \times \ln\left(\frac{t_f}{b}\right). \quad (12)$$

Although the nonzero  $\alpha$  generates the "misorientation energy"  $E_m$ , it reduces  $E_s$  at the same time. By minimizing  $E_t$  with respect to  $\alpha$ , a solution  $\alpha_{min}$ , corresponding to the misorientation angle at the equilibrium state, can be obtained in principle. The numerical result has not been obtained, but the solution is nonzero in general. The film thus will be misoriented in general (even though its stress state may in fact be metastable with respect to the formation of misfit dislocations).

## CONCLUSION

There is a misorientation between the  $\langle 111 \rangle$  directions of the substrate Si and the epitaxial  $\text{CoSi}_2$  film grown on the (111)Si when the Si surface normal,  $\hat{n}$ , is offset by an angle  $\phi_s$  against its  $\langle 111 \rangle$  direction. In our samples, the surface normal is tilted in the Si  $\langle 1\bar{1}0 \rangle$  direction. We find that all three vectors,  $\hat{n}$ ,  $\langle 111 \rangle_s$ ,  $\langle 111 \rangle_f$ , lie in the same (112) plane. The vector  $\langle 111 \rangle_f$  is always between the vectors  $\langle 111 \rangle_s$  and  $\hat{n}$ ; the angle  $\alpha$  is much smaller than  $\phi_s$ . The magnitude of the misorientation angle  $\alpha$  depends on that of the angle  $\phi_s$ , and on the average perpendicular strain,  $\epsilon^\perp$ . A simple geometrical model predicts that  $\alpha = \epsilon^\perp \times \tan \phi_s$ , which fits the experimental data very well.

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